



**DECLARATION UNDER 37 CFR 1.68**

I, Albert Josif, declare

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That I am registered U.S. Patent Agent (Reg. No. 22,917);

That I am familiar with Italian and English languages;

That I am a Sworn Translator, appointed by the Court of Milan, Italy;

That I have prepared the attached translation of the Italian Application  
No. BO2002A000759 filed on December 4, 2002 with the title:

"METHOD FOR STORING INFORMATION AT ULTRA-HIGH DENSITY ON  
THIN FILMS OF BISTABLE MOLECULES"

this Italian-language document having been filed at WIPO on May 25, 2004 in  
support of the priority rights claimed in PCT/EP03/13594;

That said translation is complete and accurate and fairly reflects the  
meaning and content of said Italian-language document;

I further declare that all statements made herein of my own knowledge  
are true and that all statements made on information and belief are believed to  
be true and further that these statements were made with the knowledge that  
wilful false statement and the like so made are punishable by fine or  
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Albert JOSIF

Milan, June 28, 2007

ITALY



## METHOD FOR STORING INFORMATION AT ULTRA-HIGH DENSITY ON THIN FILMS OF BISTABLE MOLECULES

The present invention describes a process for writing information at ultra-high density by fabricating strings of nanometer-size structures (nanostructures) constituted by bistable organic molecules known as rotaxanes. The possibility of writing information on thin films of rotaxanes in the form of regularly spaced nanostructure strings is demonstrated. The minimum demonstrated periodicity is 100 nm, the width is 40 nm, the height is a few nm. The demonstrated areal density writing is 10-100 GBits/in<sup>2</sup> (Gbps). Writing was performed on an area of tens of thousands of  $\mu\text{m}^2$ , exclusively due to instrumental limitations.

The field of application of the present invention is the field of media for storing information at ultra-high density. The main sectors of application in this field are a) backup systems and b) consumer electronics.

The invention allows one to store nonvolatile information on a soft material with a density which is comparable or superior to background art technologies and at extremely low cost. The Blu-Ray optical disc (DVD technology, but with a blue semiconductor laser instead of a red one), developed by a consortium of nine large consumer electronics industries, reaches an areal density of 10-20 Gbps. The main competition to Blu-Ray technology are holographic techniques, which are extensively protected by IBM patents. Presently, these systems have not proved themselves sufficiently stable at ambient temperature. In the case of magnetic technologies (hard disks), Nanomagnetics has demonstrated 12 Gbps, while 50 Gbps is the the short-term goal. Seagate has demonstrated 100 Gbps storage with perpendicular HDD architecture, which might enter production in 2004.

Other applications of the present invention are flash memories for cellular telephones, disposable logic circuits and devices, and identification.

These and other aims, which will become better apparent by reading

the description that follows, are achieved by a process and a material as defined in the claims.

## BACKGROUND ART

5        New technologies for data and information storage have the goal of achieving one terabit per square inch (Tbpsi), i.e., the writing of one thousand billion bits per square inch.

      Magnetic hard disks (hard disk drives, HDD) are currently the dominant technology for data storage. The maximum storage areal density  
10    demonstrated in HDD with perpendicular architecture is 100 gigabits per square inch (Gbps). Currently, commercial HDDs have a capacity of less than 50 Gbps. Although in recent years there has been an increase in the bit density in HDDs equal to 60-100% per year, it is believed that the limit of 100 gigabits per square inch cannot be exceeded with magnetic technology.  
15    Beyond this limit, the effects of superparamagnetic currents might introduce uncertainty in magnetic reading/writing density.

      Various information writing methods alternative to HDDs, which might allow to reach the Tbpsi limit and at the same time keep the dissipated power comparable to that of magnetic systems, have been proposed.  
20    Scanning probe microscopes (SPM) have been used as instruments for writing/reading data on various surfaces. The bits can be constituted by point like discontinuities on likewise flat surfaces, such as for example indentations or protrusions. The extremely high lateral resolution of SPM microscopes allows to write/read nanostructures with a density of one bit  
25    per square nm, which corresponds to hundreds of terabits per square inch. This formidable density can be achieved on atomically flat surfaces of individual crystals and by using ultra-high vacuum conditions, which are not technologically interesting. Moreover, SPM microscopes operate in a typically serial manner, and the data write/read speed is limited by the  
30    scanning speed of the tip on the surface. For a single-tip SPM, the maximum

reading speed is 50 kilobits per second (1 Mb/s in reading). The low data rate makes the SPM method too slow for mass writing.

Over the last decade, a parallel method based on SPM has been developed at the IBM Zürich research laboratories. This method is a thermomechanical process performed with an array device with multiple cantilevers, known as "millipede". Each cantilever of the millipede can be addressed individually and integrates a resistive tip, which is capable of generating heat when an appropriate voltage is applied to it. Writing occurs by indentation of the hot tip in a thermoplastic polymeric film. Said film undergoes deformation, generating a pit (one bit). The reading process occurs by measuring the difference between the heat dissipated when the tip passes over a pit with respect to the heat dissipated on the non-indented film. The many levers that write and/or read simultaneously make this technique parallel and applicable on a large area. The speed is inversely proportional to the indentation time and directly proportional to the number of levers. It has been demonstrated that this process can bear writing/reading speeds of 1-2 megabytes per second with thousands of levers in the millipede. The low power values required for the process (approximately 100 mW), due to the small displacements and to the extremely small volume of the bit, make this process competitive with respect to traditional magnetic writing in the field of flash memories. The disadvantages of millipede technology are several: each individual lever can only write a single bit at a time, the presence of malfunctioning levers generates areas which are not accessible, and the flatness of the polymeric film is critical, since the millipede is a passive system without feedback.

Other SPM processes allow to write information by generating point-like nanostructures on a flat surface. Among these, the technique that has reached the highest areal density is local oxidation of a silicon surface coated with native oxide by using a conducting AFM tip. This technique can write and read nanostructures which are 1 nm high, 20 nm wide and 50 nm

apart. The irreversible nature of the oxidation process causes this storage technique to be nonrewritable.

The aim of the present invention is to use multistable molecular thin films, which can be converted in a controlled manner among different configurations of comparable energy, to write information. Multistability is inherently present in a wide variety of molecular and supramolecular systems and becomes apparent through a variety of properties (conformations, co-conformations, oxidation states, spin momentum, shapes and dimensions, morphology). Conversion among states can be induced by mechanical, electrical, thermal, radiative external stimuli. These changes usually manifest themselves at the level of individual molecules or aggregates of a few molecules. In the case of the invention described hereinafter, these changes are transduced and amplified on larger spatial scales in order to be read.

The information storage medium is constituted by a thin film of bistable molecules known as rotaxanes. Rotaxanes are molecules constituted by a macrocycle which is closed around a linear chain and is locked on the chain by two groups with high steric hindrance. Examples of rotaxanes used for the demonstration of the process are shown in the diagram of Figure 1. Their synthesis is described in various publications of one of the inventors (DAL). Various studies, especially in solution, demonstrate the multistability of the co-conformations of this class of molecules. The architecture of rotaxanes, which is similar to an abacus, has suggested that they can be used as machines and molecular switches in the solid state. Control of molecular switches in the solid state is one possible way of writing information, provided that its effects are amplified or transduced at larger spatial scales. Other bistable molecules which could be used in a manner similar to rotaxanes are catenanes, in which two macrocycles are mutually interconnected.

The invention described hereinafter consists of a collective process

which allows one to write in a controlled, reproducible manner and at welldefined positions nanostructures on a film of rotaxanes. The process allows one to obtain storage densities on the order of 100 Gbps for thin films with a thickness of less than 5 nm. A further innovation of the method  
5 consists in the fact that the nanostructures are written simultaneously and not individually as occurs in the case of SPM technologies.

The nanostructure formation (and therefore bit writing) mechanism involves a collective molecular reorganization induced by a localized external perturbation. The localized perturbation provides the molecules in  
10 the thin film with the energy to reorganize themselves. The dimension and distance between the nanostructures depend on the thickness of the film and on the area on which the perturbation acts, but does not depend on the type of perturbation source.

The process is demonstrated by using a mechanical perturbation  
15 generated by means of an atomic force microscope (AFM) with linear scanning and therefore, in this meaning, it has the typical limitations in terms of data rate of SPM techniques. However, the process lends itself to be rescaled to the millipede technique, or more simply and effectively to any source of multiple perturbations, such as a stamp. The effectiveness of the  
20 process is demonstrated by using a stamp whose patterns are constituted by a series of parallel lines.

This process can be used to write memories of the nonvolatile type or in recordable disks with densities 10 times higher than state-of-the-art DVD technology. Other strong features of the present invention are the low cost  
25 of the materials and the simplicity of the formation of the thin films. The use of soft material makes possible to transfer the medium also to flexible and unconventional media.

The main patents which relate to different types of process for writing memories on organic thin films are:

30 – Chou, US patent 5,772,905; June 30, 1998; “Nanoimprint

lithography”

- Binnig et al., US patent 5,835,477; November 10, 1998; "Mass Storage Application of Local Probe Arrays"
- Sandhu et al., US patent 6,358,756; March 19, 2002; "Self-aligned, magnetoresistive random-access memory (MRAM) structure utilizing a spacer containment scheme"
- Zhou et al., US patent 6,222,755; April 24, 2001; "Solid-state holographic memory"
- Hua et al., US patent 6,214,431; April 10, 2001; "Optical data storage materials for blue-light DVD-R"
- Cavallini and Biscarini, Italian patent no. MI2002A001961, September 16, 2002: "Procedimento per la fabbricazione ed il controllo mediante stampaggio su scale micro- e nanometriche di strutture e motivi di sostanze solubili e colloidali con riduzione delle dimensioni dei motivi dello stampo".

## ANALYSIS OF THE RESULT

The present invention is based on a new physical phenomenon which can be induced and controlled in thin films of rotaxanes by means of a localized perturbation. The perturbation, which in this case is mechanical, is a dissipative force which acts on the thin film in spatially defined regions. Below this force, nothing happens to the film. Above this force, the film is damaged. The effect of this local perturbation is to induce a reorganization of the molecules, which manifests itself as a local change of morphology. When the perturbation occurs along a line (for example an AFM tip which moves in a linear scan), this change generates nanostructures which self-organize along said line. The nanostructures are characterized by specific spacings and dimensions, which are controlled by the thickness of the film. The number of nanostructures is regulated by the length of the line which is subjected to the perturbation.

In the process of the present invention, the writing medium is a thin film of rotaxanes deposited on a substrate, which can be taken among various materials: highly oriented pyrolytic graphite, mica, metals, polymers, silicon, glass, indium-tin oxide (ITO), perovskite oxide (manganites). Film deposition can be performed with any technique which allows one to control of the thickness of the film on a large area: deposition from solution, spin casting, evaporation in vacuum or ultrahigh vacuum, self-assembling.

The process is demonstrated for films with a thickness comprised between 3 and 35 nm, and its application to any other thickness is in any case valid. A film of rotaxanes prepared appropriately has a uniform appearance on its entire surface and low roughness (rms roughness <2 nm). The film is stable in ambient conditions (in air at ambient temperature and humidity, exposed to the light). Morphological investigation with an AFM reveals that a thin film prepared six months earlier shows no difference with respect to a freshly made film.

#### DESCRIPTION OF THE DYNAMIC PROCESS

The film can be observed with an AFM microscope in contact mode by using load forces lower than a threshold value which is typically estimated at 2 nN. This threshold value may depend on the type of tip used and on its possible contamination. By applying load forces just above the threshold value, a mechanical perturbation is caused, the effect whereof is localized to the area of contact of the tip. By passing the tip several times along the line, the energy transferred from the tip to the film by friction produces a morphological transition which becomes manifest with the onset of nanostructures which are equally spaced along the line. The result is that the tip writes strings of regularly spaced nanostructures. This process is shown schematically in Figure 2.

Typically, to complete the process, by using silicon nitride tips, 4 to 20 scans are required for a frequency comprised between 1 and 5 Hz. The



decisive parameter is the dwelling time of the tip in contact with the film, and accordingly the use of higher scanning rates requires a larger number of scans. The transformation time is calculated as on the order of a few tens of microseconds. Once the transformation is complete, the further scanning of the tips on the nanostructures no longer causes any change. The following phenomenological law is given which links the number of scans to the scan rate valid for a non-contaminated silicon nitride tip by applying thereto a force which is equal to the threshold force:

$$\text{const} = n\nu$$

where  $n$  is the number of scans and  $\nu$  is the scan rate expressed in Hz.

By raising the load force above 4 nN, the film is damaged irreversibly by removing material.

Figure 3 illustrates some examples of writing of nanostructures on a surface of thin films, using the type 1 molecule (see scheme of Figure 1) on a graphite substrate.

Figure 3a illustrates a grid of nanostructures which are 35 nm wide and are arranged on a square grid which has a spacing of 140 nm. This grid was generated on a film with a thickness of 5 nm by performing scans in the writing conditions described above along individual and mutually parallel lines.

Figure 3b illustrates the application of the writing process to an area of  $30 \times 30 \mu\text{m}^2$ , with 31 lines of 45 nanostructures each. Furthermore, the image shows that the presence of the typical surface defects, including terraces, does not compromise the process. This area is limited in the specific case by the maximum scanning dimensions of the piezoelectric positioning unit mounted on the AFM. Therefore, the writing process is suitable to be extended to large areas.

Figure 3c is an AFM image of a thin film with a thickness of 25 nm, and the number of nanostructures is directly proportional to the length of the line where the perturbation acts.

Figure 3d demonstrates the application in the writing of an item of information on the film; in particular, the sequence of nanostructures "e-c-7-a-8" has been written in hexadecimal language, and corresponds to the number 968616.

5 Figure 4 illustrates explicitly the linear relationship between the number of nanostructures and the length of the perturbed line as in Figure 3c. This implies that once the thickness of the film has been set, the number of nanostructures can be predetermined precisely on the basis of the length of the scan line. The linear relationship is of the type  $N = aL$ , where  $N$  is the  
 10 number of nanostructures and  $L$  is the length of the perturbed line. In the example of Figure 4, the best linear fit provides  $N = 0.453 (\pm 0.006 \mu\text{m}^{-1}) L$ . The exact value depends on the thickness of the thin film. The error on the number of nanostructures is calculated by error propagation, and therefore  $\Delta N = \Delta aL + L\Delta a$ . The second term is negligible because of the accuracy of  
 15 the lateral positioning in an AFM (which is limited by the D/A converter that drives the piezoelectric actuator, typically of the 18-bit type). Accordingly,  $\Delta N/N = \Delta a/a = 1.32 < 2\%$ . Therefore, writing accuracy is better than 2%.

Figure 5 illustrates the values of the spacing between the  
 20 nanostructures, the diameter of the nanostructures and the thickness of the nanostructures as a function of the thickness of the film in the case of the rotaxane 1 grown on graphite. The size and spacing of the nanostructures depend in a linear fashion on the thickness of the film:

$$P = \alpha D; R = \beta D; h = \gamma D$$

25 where  $D$  is the thickness of the film,  $P$  is the spacing (characteristic distance) between the nanostructures,  $R$  is the diameter of the nanostructures, and  $h$  is the height of the nanostructures with respect to the unperturbed film. The thinnest films that we have been able to provide measure 3 nm and provide structures with  $R = 20$  nm,  $h = 1.5$  nm, and  
 30  $P = 110$  nm. The estimated error on statistics of approximately 100

nanostructures is 10-20%. For a rotaxane monolayer with a thickness of approximately 1 nm, one can expect a periodicity of approximately 90 nm on the basis of the extrapolation of Figure 5. This would correspond to a maximum write density of approximately 80 Gbps.

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## DESCRIPTION OF THE STATIC PROCESS

The mechanical perturbation that provides the energy required for the reorganization that leads to the appearance of the nanostructures can also be induced statically by means of a stamp.

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The process is shown schematically in Figure 6. The stamp is placed in contact with the rotaxane film and then an appropriate pressure (on the order of 1 kg/cm<sup>2</sup>) is applied. The process time, estimated in a few seconds, depends on the material of the stamp, on the size of the motifs of the stamp, on the thickness of the film and on the particular type of rotaxane used. The writing speed with the static method depends also on the size of the motifs of the stamp.

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In Figure 7, the atomic force microscope image shows the result of the morphological reorganization following the static process. The process is applied to a rotaxane film / deposited on graphite. The stamp consists of a sequence of parallel lines which are 400 nm wide and 100 nm thick and are covered by a thin gold film. The applied pressure is 2.5 kg/cm<sup>2</sup>. The result is that at the protrusions, i.e., where the stamp applies the load force to the film, the film is transformed, producing a sequence of nanostructures along the entire length of the lines of the stamp. By manufacturing suitable stamps with lines of different length it is possible therefore to generate different numbers of nanostructures along each line, according to the respective length, and thus modulate the information spatially.

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The application of the static method therefore allows one to transfer in a few seconds the entire information contained in a disk, with a resolution potentially on the order of 100 nm. With a stamp measuring 1 square inch,

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patterned with a density which is comparable to that of a DVD, i.e., approximately 5 Gbps, and a printing time of 5-10 seconds, one might reach writing speeds for nonvolatile memories of 0.1-1 Gbit/s. This writing speed is higher than any currently existing technology.

- 5 Both in the static case and in the dynamical case, the process was observed with rotaxanes and not with the respective separate components (thread and macrocycle). The origin of the particular behavior of the rotaxanes is explained by calculating structural energies. Computer simulation of the energy of rotaxanes in the solid state shows that rotaxanes  
10 exist in the solid state in multiple structures characterized by a minimal difference ( $<10 \text{ kJmol}^{-1}$ ) in energy. The energy required for their interconversion (i.e., the energy of transition state ETS) is on the same order of magnitude as the packing energy EI (for example rotaxane 1: ETS =  $200 \text{ KJmol}^{-1}$  and EI =  $230 \text{ KJmol}^{-1}$ ). In other words, it has been demonstrated that  
15 rotaxanes can interconvert in the solid-state, exposing to the surface various crystalline surfaces without destruction of the condensed phase. The formation mechanism of the nanostructures is therefore as follows:
- i) the rotaxane film is initially amorphous.
  - ii) the mechanical perturbation provides the energy to allow the  
20 molecules along a line to organize themselves in the crystalline nuclei, exposing the most stable surface.
  - iii) the crystallites grow and incorporate smaller nuclei and nearby molecules within a minimum distance, providing larger crystallites.
  - iv) the nanostructures emerge when the expansion of the crystallites  
25 reaches a critical size. This entails also the onset of a characteristic distance. The nanostructures are completed by incorporation of molecules with high diffusivity, which are the ones stimulated along the line.

It is important to stress that only the molecules subjected to the perturbation contribute to the process, and therefore the effect of the  
30 reorganization is extremely localized.